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# Hydrogen-Bonded Aryl Amide Macrocycles: Synthesis, Single-Crystal Structures, and Stacking Interactions with Fullerenes and Coronene

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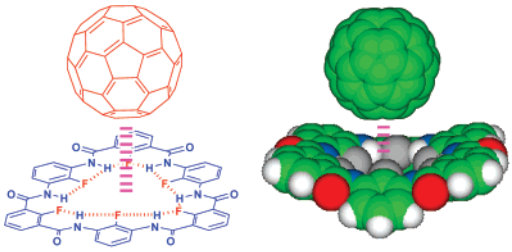

Six hydrogen-bonded shape-persistent aryl amide macrocycles have been prepared by using one-step and (for some) step-by-step approaches. From the one-step reactions, 3 + 3, 2 + 2, or even 1 + 1 macrocycles were obtained in modest to good yields. The reaction selectivity was highly dependent on the structures of the precursors. The X-ray structural analysis of two methoxyl-bearing macrocycles revealed intramolecular hydrogen bonding and weak intermolecular stacking interaction; no column-styled stacking structures were observed. The $^1$H (DOSY) NMR, UV−vis, and fluorescent experiments indicated that the new rigidified macrocycles complex fullerenes or coronene in chloroform through intermolecular $\pi$-stacking interaction. The association constants of the corresponding 1:1 complexes have been determined if the stacking was able to cause important fluorescent quenching of the macrocycles or coronene.

## Introduction

Shape-persistent macrocycles have received considerable attention for their unique structures, properties, and applications in supramolecular and materials chemistry.[1,2] Many of these rigidified molecules are developed based on the oligomeric *m*-aryleneethynylene skeletons,[3] which are usually prepared by transition metal-catalyzed multistep coupling reactions. More recently, one-step preparation of shape-persistent aryl amide or urea macrocycles has been reported from hydrogen bonding-mediated monomers.[4,5] The high efficiency of such an approach is greatly attributed to the preorganized folded conformations of the intermediates, which are stabilized by successive intramolecular hydrogen bonding. In addition, some of the macrocycles have been revealed to be capable of binding guanidinium ions or DNA G-quadruplex through intermolecular hydrogen bonding or stacking interaction.[4b,5a]

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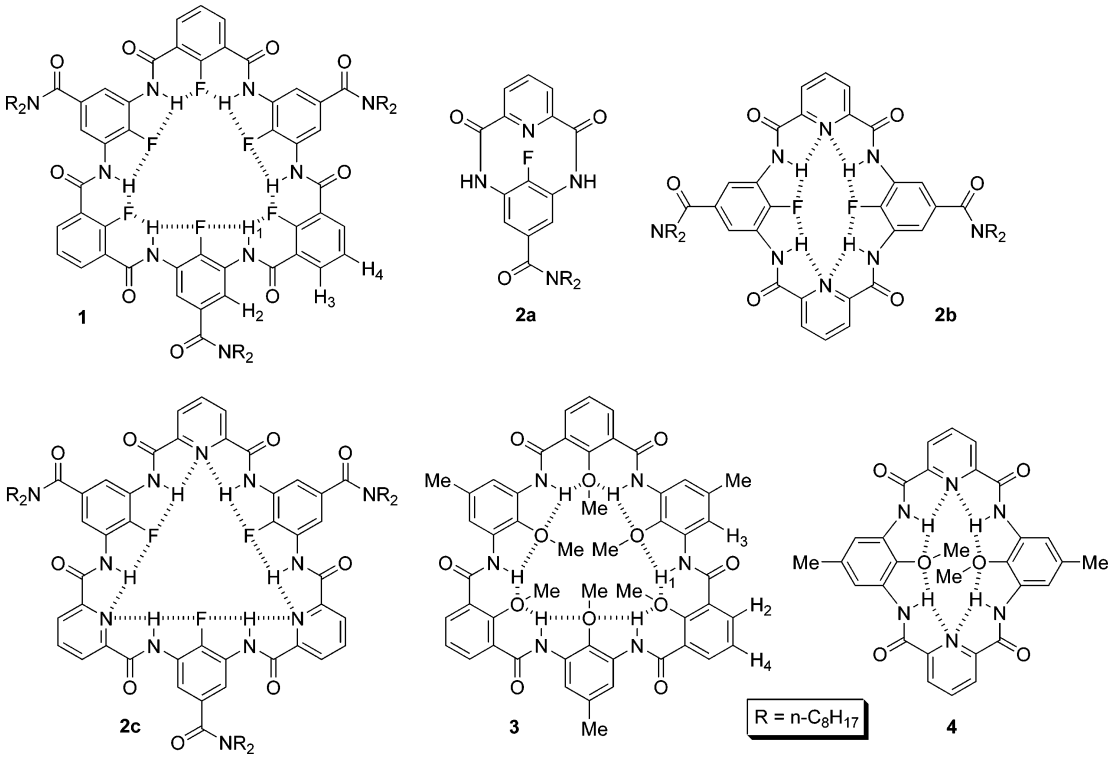
**CHART 1**




We recently demonstrated that hydrogen bonding-induced aryl amide or hydrazide foldamers could function as new synthetic receptors for binding neutral and ionic species or preorganized scaffolds for assembling well-defined architectures.[6,7] We also found that several folded structures resembled the extended conjugated systems, such as porphyrins, phthalocyanines, or rigidified phenylene−acetylene macrocycle,[8,9] to stack with fullerenes in both the solution and solid state.[10] In search of new compact synthetic receptors,[11] we became interested in preparing new hydrogen bonding-mediated aryl amide macrocycles. We herein describe the synthesis of six new aryl amide macrocycles and their stacking behaviors with fullerenes and conorene.

## Results and Discussion

We have previously established the intramolecular five- and six-membered F···H−N hydrogen-bonding motif and utilized it to direct folded or helical conformation of aryl amide oligomers.[7d,10,12] Different from the MeO···H−N hydrogen-bonded folded structures,[6a,7e,i] in which the inwardly located methyl groups were deviated from the rigidified backbones due to the steric hindrance and intrinsic angular requirement of the ether bonds, the F···H−N hydrogen-bonded foldamers possessed more planar extended skeletons. To compare the efficiency of discrete hydrogen-bonding motifs in directing macrocyclization and also to explore their possible influence on the structures of the resulting macrocycles, we used the one-step method to prepare macrocycles from the reactions of the corresponding diacyl chlorides and diamines.[4,5] To our surprise, macrocycles **1**−**4** with a changing number of segments were obtained (Chart 1).

Mixing the identical molar equiv of compounds **5**[7e] and **6**[13] (38 mM) in THF in the presence of triethylamine at room temperature led to the formation of 3 + 3 macrocycle **1** in 40% yield as the sole isolated product (Scheme 1).[14] In contrast, under the identical conditions, the reaction of **5** with **7** (1:1, 38 mM) afforded three macrocyclic products **2a**, **2b**, and **2c** in 10%, 40%, and 30% yields, respectively. The formation of the smaller 1 + 1 and 2 + 2 products should reflect the shrunk shape of pyridine relative to that of benzene.[4,12b] The reaction of diamine **8** with **9** (1:1, 38 mM) gave rise to the expected 3 + 3 product

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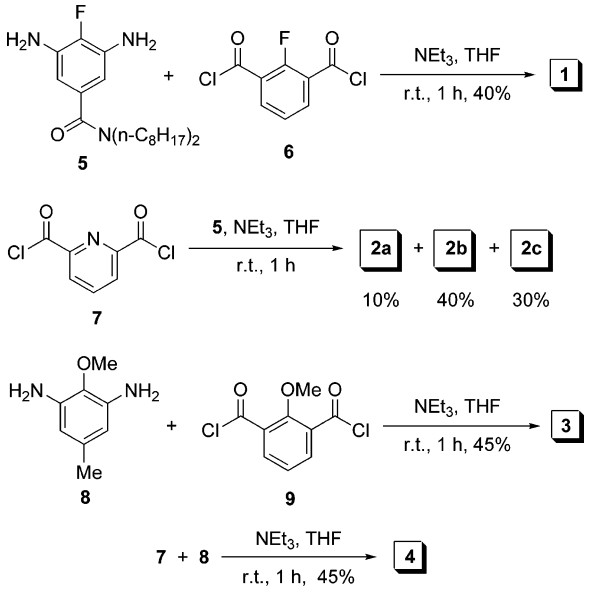
(14) Under the identical conditions, a similar 3 + 3 macrocyclic product was also generated from the reaction of **5** with isophthaloyl dichloride, as evidenced by MALDI-TOF. The attempt of separating this product did not succeed. We thank one of the reviewers for critical comments on this issue.

**SCHEME 1**



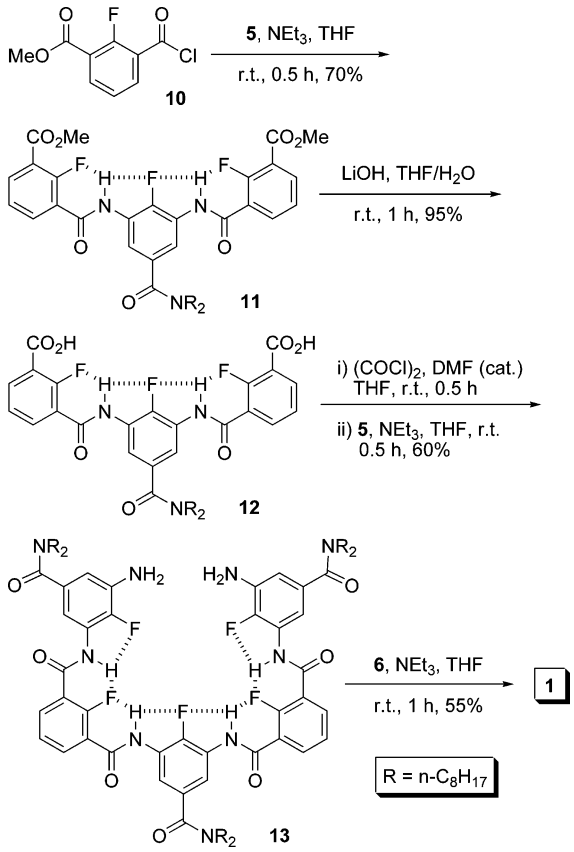

**3** in 45% yield. However, its reaction with pyridine derivative **7** of the same concentration (38 mM) afforded 2 + 2 compound **4** as the sole macrocycle. The introduction of the *N*,*N*-di-*n*-octylamide groups rendered compounds **1** and **2** good solubility in organic solvents. It is noteworthy that, with less polar dichloromethane or chloroform as solvent,[4,5] the macrocycles could also be prepared. Nevertheless, the yields of the products, usually 10−15%, were pronouncedly decreased. When the reactions were conducted at lower concentrations, the yields of the macrocycles were increased modestly. For example, compound **1** was obtained in 45−52% yields when the concentrations of **5** and **6** were reduced to the range of 20 to 3.5 mM.

Compounds **2a**, **2b**, and **2c** were separated by careful column chromatography. Due to their structural symmetry, their $^1$H NMR spectra in $CDCl_3$ all exhibited four signals in the downfield area. The signal of the amide protons appeared at 9.99, 10.55, and 9.61 ppm, respectively. CPK (Corey−Pauling−Koltun) modeling showed that the amide units of **2a** take the trans conformation as a result of the small size of the backbone and no intramolecular hydrogen bonds are formed. No similar products were obtained from the reactions of **6** or **9**. Therefore, its formation should be attributed to the small spatial hindrance and shrunk conformation of the pyridine unit.

To explore the influence of the different hydrogen-bonding motifs on the macrocyclization, compounds **1** and **2c** were also prepared by using the step-by-step approach. The synthetic routes are provided in Schemes 2 and 3, respectively. As expected, the yields of the cyclization reactions were higher than those of the above one-step reactions, because only two amide bonds were formed in these reactions. The yields of the macrocyclization reactions are also quite close, implying that the F···H−N and N···H−N hydrogen-bonding motifs in the precursors have comparable capacity in directing the macrocyclization.

Macrocycles **1**−**4** have been characterized by the $^1$H and $^{13}$C NMR spectroscopy and (high resolution) mass spectrometry or X-ray single crystal analysis. Due to the high structural symmetry, the $^1$H NMR spectra of all the macromolecules in $CDCl_3$ displayed one signal for the amide protons at the downfield area, supporting that they were involved in intramolecular

**SCHEME 2**




hydrogen bonding. Diluting the solution of the macrocycles in chloroform-*d* from 5.0 to 0.2 mM did not cause salient change of their chemical shifts, indicating that there was no significant intermolecular hydrogen bonding or aromatic stacking. The NH signals of **2a**, **2b**, and **2c** appeared at 9.99, 10.55, and 9.61 ppm, respectively, in the $^1$H NMR spectra (5 mM). The fact that **2b** displayed a substantially large chemical shift suggested that this macrocycle had a low intramolecular tension and consequently strong hydrogen bonds, which is also consistent with its high yield relative to those of **2a** and **2c**.

After numerous attempts to crystallize the macrocycles, single crystals of **3** and **4** suitable for X-ray analysis were grown by slow evaporation of their chloroform−ethyl acetate solution. Their solid state structures are provided in Figures 1 and 2. As expected, the amide protons of both compounds are involved in intramolecular three-center hydrogen bonding. No column-styled stacking was observed in the solid state structures,[15] possibly because the methyl groups prevented intermolecular face-to-face stacking. For macrocycle **3**, four adjacent methyl groups were located on one side of the backbone, while another two pointed to the other side. One of the diamidobenzene units stacked with the identical unit of another molecule, giving rise to an extended slip-styled array structure (Figure 1). In the solid state of **4** (Figure 2), the two interior methyl groups pointed to both sides of the backbone, respectively. The two pyridine rings were orientated in one plane and the two benzene rings deviated from the plane considerably. As a result, a chair-styled

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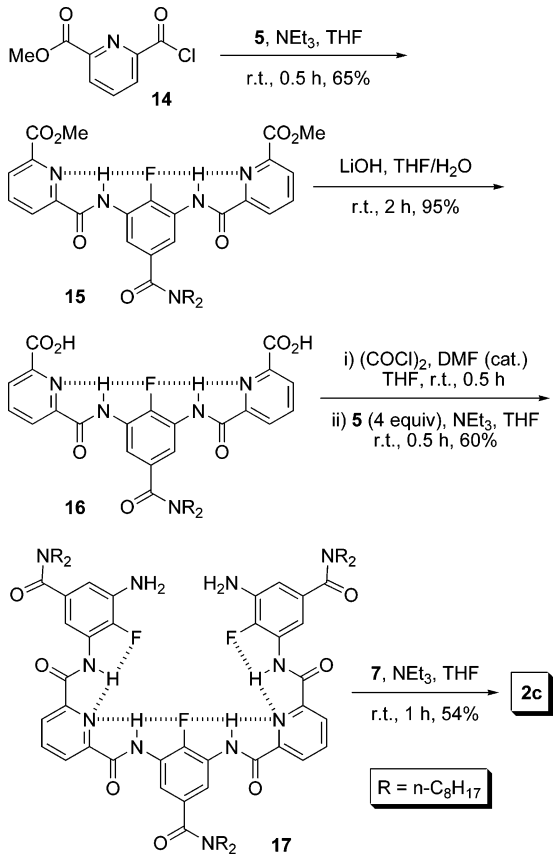
**SCHEME 3**




conformation was produced. Extended array structures were formed by intermolecular pyridine−pyridine stacking, but no aromatic stacking was observed for the diamidobenzene units, which may be attributed to the steric effect of the inwardly located methyl groups. The fact that no two- or six-residue macrocycle was produced from the reaction of **7** with **8** indicated that (1) the shrunk shape of the 2,6-disubstituted pyridine unit was favorable for the formation the 2 + 2 product and (2) the larger methoxyl group in **8** suppressed the formation of the even smaller 1 + 1 macrocycle similar to **2a**, which were in

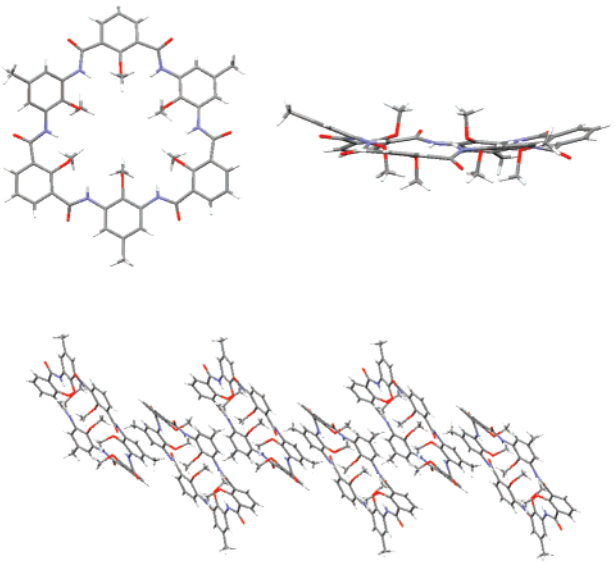


**FIGURE 1.** The solid state of 3 + 3 macrocycle **3**.

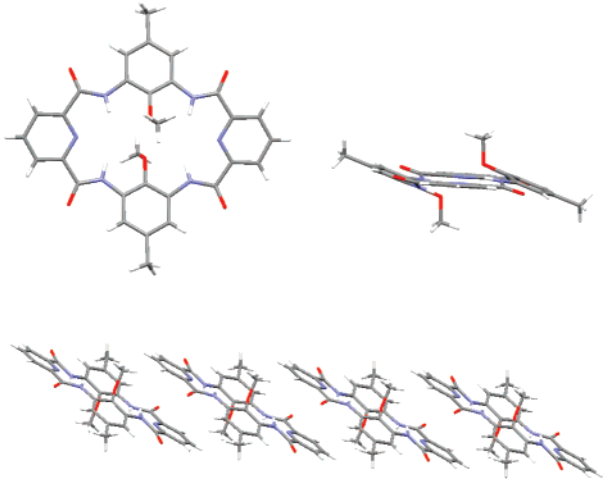


**FIGURE 2.** The solid state of 2 + 2 macrocycle **4**.

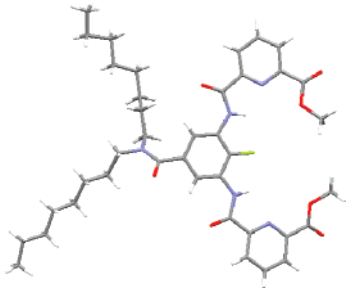


**FIGURE 3.** The solid state of compound **15**.

accordance with the above result. These observations clearly revealed the great influence of the size of the hydrogen-bonded groups on the distribution of the products. The solid state structure of intermediate **15** is provided in Figure 3. The hydrogen-bonded N···H distance is 2.249 Å, which is very close to the value of 2.254 Å for that of macrocycle **4**. Since no intramolecular spatial repulsion was observed for **15**, this observation also implied that no large skeleton tension existed in **4** and the 2,6-diaminopyridine derivatives preferred to form more compact folded or macrocyclic structures.[16]

It is well-established that rigidified macrocycles are able to stack intermolecularly.[17] Our recent study also revealed that some of the hydrogen bonding-induced foldamers have a great tendency to stack with fullerenes in both the solution and solid states.[10] The possibility of a similar interaction between the new rigidified macrocycles and fullerenes was therefore explored with the $^1$H NMR experiments. Adding 1 equiv of $C_{60}$ to the solution of **1** (5 mM) in $CS_2$−$CDCl_3$ (1:2 v/v) caused small but distinct downfield shifting for the NH signal (Figure 4).[18,19] Similar shifting was also observed for the mixture of **1** and $C_{70}$. The chemical shifts for the signals in the downfield region in the absence and presence of fullerenes are listed in Table 1 (vide infra). These observations were consistent with those revealed

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(18) $CS_2$ was used for improving the solubility of fullerenes.

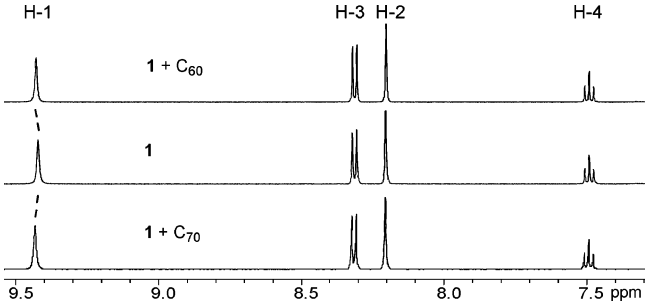


**FIGURE 4.** The downfield region of the $^1$H NMR spectra (500 MHz) of the solutions of **1** + $C_{60}$, **1**, and **1** + $C_{70}$ in $CDCl_3$ at 25 °C (5 mM).

**TABLE 1. Diffusion Coefficients of 1 and 3 in the Absence and Presence of Fullerenes (1:1, 5 mM), Probed with Their Downfield Signals in $CDCl_3$ and $CS_2$ (1:1, v/v)**

| | **1** | | **1** + $C_{60}$ | | **1** + $C_{70}$ | |
|---|---|---|---|---|---|---|
| proton | $\delta$ (ppm) | $D$ ($10^{-9}$ m$^2$/s) | $\delta$ (ppm) | $D$ ($10^{-9}$ m$^2$/s) | $\delta$ (ppm) | $D$ ($10^{-9}$ m$^2$/s) |
| H-1 | 8.962 | 10.66 | 8.965 | 8.57 | 8.966 | 9.72 |
| H-2 | 8.173 | 10.97 | 8.171 | 8.88 | 8.170 | 10.02 |
| H-3 | 8.057 | 11.23 | 8.057 | 8.88 | 8.058 | 10.12 |
| H-4 | 7.271 | 11.58 | 7.272 | 8.95 | 7.275 | 10.27 |
| | **3** | | **3** + $C_{60}$ | | **3** + $C_{70}$ | |
| proton | $\delta$ (ppm) | $D$ ($10^{-9}$ m$^2$/s) | $\delta$ (ppm) | $D$ ($10^{-9}$ m$^2$/s) | $\delta$ (ppm) | $D$ ($10^{-9}$ m$^2$/s) |
| H-1 | 9.404 | 11.88 | 9.400 | 6.98 | 9.404 | 7.08 |
| H-2 | 8.295 | 12.32 | 8.295 | 7.43 | 8.292 | 7.16 |
| H-3 | 8.177 | 12.57 | 8.175 | 7.37 | 8.176 | 7.22 |
| H-4 | 7.463 | 11.98 | 7.462 | 7.30 | 7.463 | 7.00 |

for F···H−N hydrogen-bonded foldamers and fullerenes and supported intermolecular interactions also existed between the macrocycle and the fullerenes.[10] Under the identical conditions, smaller or no shifting was observed for the signals of **2**−**4** in the presence of $C_{60}$ or $C_{70}$.

More solid evidence came from the diffusion-ordered spectroscopic (DOSY) experiments in $CDCl_3$ and $CS_2$ (1:1, v/v).[20,21] The diffusion coefficients ($D$) obtained for macrocycles **1** and **3** in the absence and presence of $C_{60}$ or $C_{70}$ are presented in Table 1. It can be found that the presence of $C_{60}$ or $C_{70}$ led to significant and consistent decrease of the $D$ values of the macrocycles probed with all their four signals at the downfield area. Moreover, the values of the same systems obtained with different probes displayed a similar changing tendency. All these observations supported that close proximity took place for the two species (Figure 5), leading to an increase of the apparent size or molecular weight of the macrocycles. Under the identical conditions, the addition of fullerenes could only produce remarkably smaller change for the diffusion coefficients of **2a**, **2b**, **2c**, and **4**, implying that their interactions with these cyclophanes were much weaker.

Adding $C_{60}$ or $C_{70}$ to the solution of **1** or **3** in chloroform also caused significant decrease of the absorption bands of the macrocycles (see the Supporting Information), which represents additional evidence for the formation of the stacking complexes. In addition, the emissions of both macrocycles could be quenched remarkably by fullerenes. On the base of the fluorescent titrations (Figure 6), we determined the association constants ($K_{assoc}$) of complexes **1**·$C_{60}$, **1**·$C_{70}$, **3**·$C_{60}$, and **3**·$C_{70}$ in chloroform to be ca. $5.9 \times 10^4$, $9.1 \times 10^4$, $2.5 \times 10^4$, and $4.1 \times 10^4$ M$^{-1}$, respectively, by using the Benesi−Hildebrand (BH) plot.[22] The values of $C_{70}$ are notably larger than those of $C_{60}$, implying that its stacking with the macrocycles mainly took place at its extended equatorial region.[8]

Because fullerenes are electron deficient,[23] it is reasonable to consider that their stacking with fluorine-bearing **1** was not driven by the electrostatic interaction. Since pyridine-incorporated **2c** did not exhibit similar capacity of strongly interacting with fullerenes, we propose that the stacking between **1** and fullerenes most likely resulted from a combination of the extended fluoroarene−$\pi$[24] and solvophobic interactions. The fact that the values of **3** were smaller than those of **1** may be simply ascribed to the steric hindrance of the six methyl groups at its central area.

The stacking behavior of the macrocycles with planar coronene (**18**) was also investigated.[25] The $^1$H NMR spectra of their 1:1 solutions in $CDCl_3$ (5 mM) displayed small shifting for their signals in the downfield area. The largest change was observed for the NH signal of **1** ($\Delta\delta = -0.023$ ppm). The emission of coronene were remarkably quenched by **2c**, **3**, and **4** (see the Supporting Information). Also on the base of the fluorescent titrations, we estimated the $K_{assoc}$ values of complexes **2c·18**, **3·18**, and **4·18** in chloroform to be $1.2 \times 10^3$, $1.8 \times 10^3$, and $9.1 \times 10^3$ M$^{-1}$, respectively. The value of **3·18** is significantly lower than that of **3**·$C_{60}$. Surprisingly, the binding affinity of smaller **4** is considerably greater than that of **2c** and **3**, which may reflect that its four aryl units could match well for interacting with coronene as a result of the reduced size. Unexpectedly, adding **1** to the solution of coronene did not lead to similar quenching for the emission of the latter. Considering the great capacity of **1** to interact with fullerenes, this result should not be used as evidence to exclude stacking interaction between **1** and coronene. We consider this may just reflect that there was no efficient intermolecular electron or energy transfer between them.

## Conclusions

We have prepared six amide-derived macrocycles that are rigidified by intramolecular hydrogen bonding. The shape or

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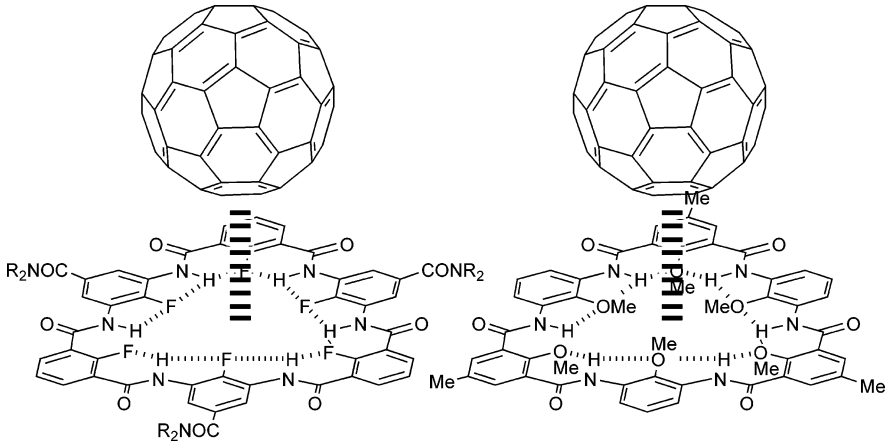

**FIGURE 5.** Stacking interaction between macrocycles **1** and **3** and $C_{60}$.

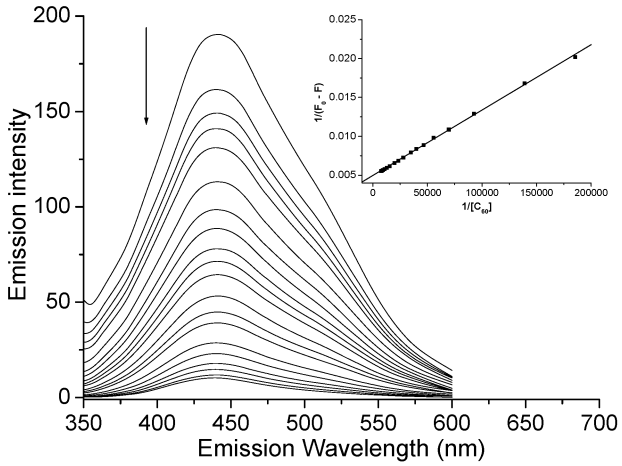


**FIGURE 6.** Fluorescent titration spectra of **1** ($3.6 \times 10^{-5}$ M) with $C_{60}$ in chloroform at 25 °C (excitation wavelength = 309 nm). Inset: The Benesi−Hildebrand (BH) plot (variation of the fluorescence intensity of **1** with the addition of $C_{60}$).

geometry of the precursors remarkably affects the structures of the products. As a result, macrocycles with 1 + 1, 2 + 2, and 3 + 3 segments can be prepared by simply changing the precursors. The stacking interaction revealed between the new macrocycles and fullerenes and coronene represents the first example of its kind observed for unconjugated aromatic amides, while the strong complexing affinity reflects the cooperativity of the aromatic units of the macrocycles in strengthening the stacking. The results provide a new avenue for self-assembling architectures and materials. We are currently trying to introduce amino or aldehyde groups to the aryl rings and expect that three-dimensional column systems will be developed by using the dynamic covalent approach.[26]

## Experimental Section

**General Procedures.** See the Supporting Information.

**Typical Procedure for the One-Step Synthesis of Macrocycles 1−4. Compound 1:** To a solution of 2-fluoroisophthalic acid (0.14 g, 0.76 mmol) in THF (20 mL) was added oxalyl dichloride (1.6 mL, 19.8 mmol) and DMF (0.05 mL). The solution was stirred at room temperature for 0.5 h and then concentrated under reduced pressure to give crude product **6** as a pale yellow solid. The material was again dissolved in THF (30 mL). The solution and a solution of **7a** (0.30 g, 0.76 mmol) in THF (30 mL) were then simultaneously added dropwise to a solution of triethylamine (0.5 mL) in THF (30 mL) at 0 °C. The mixture was stirred at room temperature for 1 h. The precipitate formed was filtered off and the filtrate concentrated under a reduced pressure. The resulting residue was triturated with chloroform (60 mL) and the organic phase washed with diluted hydrochloric acid (1 N, 20 mL), water (20 mL × 2), and brine (20 mL) and dried over sodium sulfate. After the solvent was removed, the crude product was purified by column chromatography ($CHCl_3$/AcOEt 1:1) to afford **1** as a white solid (0.17 g, 40%). Mp 222−224 °C. $^1$H NMR ($CDCl_3$) $\delta$ 8.95 (s, 6 H), 8.32 (s, 6 H), 8.11(t, $J$ = 6.0 Hz, 6 H), 7.34 (t, $J$ = 7.8 Hz), 3.30 (s, 6 H), 3.20 (s, 6.0 H), 1.28−1.17 (m, 72 H), 0.86 (s, 9 H), 0.79 (s, 9 H). $^{13}$C NMR ($CDCl_3$) $\delta$ 170.1, 161.1, 158.6, 156.1, 145.0, 142.6, 136.1, 133.5, 126.0, 125.6, 122.5, 122.3, 116.9, 49.3, 44.9, 31.9, 31.8, 29.7, 29.4, 29.2, 29.1, 28.6, 27.4, 27.1, 26.7, 22.6, 22.6, 14.1. $^{19}$F NMR ($CDCl_3$) $\delta$ −115.0 (s, 3 F), −142.6 (s, 3 F). MS (MALDI-TOF) $m/z$ 1648.6 $[M + Na]^+$, 1664.5 $[M + K]^+$. HRMS (MALDI-TOF) calcd for $C_{93}H_{124}N_9O_9F_6$ $[M]^+$ 1624.9421, found 1624.9465.

**Macrocycle 2a:** White solid. Mp 290−292 °C. $^1$H NMR ($CDCl_3$) $\delta$ 9.99 (s, 2 H), 8.40 (d, $J$ = 7.7 Hz, 2 H), 8.08 (t, $J$ = 7.8 Hz, 1 H), 7.99 (s, 2 H), 3.36 (br s, 2 H), 3.26 (br s, 2 H), 1.57 (br s, 4 H), 1.34−1.18 (m, 20 H), 0.85 (s, 3 H), 0.78 (s, 3 H). $^{13}$C NMR ($CDCl_3$) $\delta$ 169.6, 161.0, 148.4, 139.6, 133.6, 125.9, 125.7, 125.6, 117.4, 49.6, 45.3, 31.8, 29.7, 29.2, 28.8, 27.6, 27.4, 27.1, 26.7, 22.6, 14.0. $^{19}$F NMR ($CDCl_3$) $\delta$ −137.3 (s). MS (MALDI-TOF) $m/z$ 524.1 $[M + H]^+$. HRMS (MALDI-FT) calcd for $C_{30}H_{42}N_4O_3F$ $[M]^+$ 525.3236, found 525.3223.

**Macrocycle 2b:** White solid. Mp 208−210 °C. $^1$H NMR ($CDCl_3$) $\delta$ 10.55 (s, 4 H), 8.43 (d, $J$ = 7.7 Hz, 4 H), 8.22 (t, $J$ = 7.7 Hz, 2 H), 8.17 (t, $J$ = 2.8 Hz, 4 H), 3.46 (br s, 4 H), 3.25 (br s, 4 H), 1.69−1.62 (m, 8 H), 1.37−1.16 (m, 40 H), 0.92 (s, 6 H), 0.76 (s, 6 H). $^{13}$C NMR ($CDCl_3$) $\delta$ 169.7, 160.3, 148.6, 142.9, 141.6, 140.6, 135.0, 126.3, 125.5, 112.4, 49.4, 45.3, 31.8, 29.4, 29.3, 29.0, 28.7, 27.6, 27.2, 26.6, 22.7, 22.5, 14.0. $^{19}$F NMR ($CDCl_3$) $\delta$ −144.69. MS (MALDI-TOF) $m/z$ 1071.6 $[M + Na]^+$, 1049.6 $[M + H]^+$. HRMS (MALDI-FT) calcd for $C_{60}H_{83}N_8O_6F_2$ $[M]^+$ 1049.6398, found 1049.6398.

**Macrocycle 2c:** White solid. Mp 118−120 °C. $^1$H NMR ($CDCl_3$) $\delta$ 9.61 (s, 6 H), 8.46 (d, $J$ = 7.5 Hz, 6 H), 8.15 (t, $J$ = 7.8 Hz, 3 H), 7.98 (d, $J$ = 6.9 Hz, 6 H), 3.42−3.31 (m, 12 H), 1.65 (s, 12 H), 1.30−1.21 (m, 60 H), 0.86−0.81 (m, 12 H). $^{13}$C NMR ($CDCl_3$) $\delta$ 169.8, 162.1, 148.8, 139.5, 133.4, 126.2, 125.5, 120.0, 49.6, 45.1, 31.8, 29.2, 28.6, 27.5, 27.0, 26.7, 22.6, 14.1. $^{19}$F NMR ($CDCl_3$) $\delta$ −139.4 (s, 3 F). MS (MALDI-TOF) $m/z$ 1612 $[M + Na]^+$, 1596.9 $[M]^+$. HRMS (MALDI-TOF) calcd for $C_{90}H_{124}N_{12}O_9F_3$ $[M]^+$ 1573.9561, found 1573.9575.

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**Macrocycle 3:** White solid. Mp >300 °C dec. $^1$H NMR ($CDCl_3$) $\delta$ 9.49 (s, 6 H), 8.32 (d, $J$ = 7.8 Hz, 6 H), 8.22 (s, 6 H), 7.50 (t, $J$ = 7.8 Hz, 3 H), 4.06 (s, 9 H), 3.94 (s, 9 H), 2.45 (s, 9 H). $^{13}$C NMR ($CDCl_3$) $\delta$ 162.7, 155.2, 136.7, 136.0, 135.8, 130.8, 128.1, 126.2, 118.0, 64.6, 61.5, 21.9. MS (MALDI-TOF) $m/z$ 959.4 [M + Na]$^+$. HRMS (MALDI-FT) calcd for $C_{51}H_{48}N_6O_{12}Na$ [M]$^+$ 959.3222, found 959.3259.

**Macrocycle 4:** White solid. Mp >300 °C dec. $^1$H NMR ($CDCl_3$) $\delta$ 10.79 (s, 4 H), 8.46 (d, $J$ = 7.5 Hz, 4 H), 8.23 (t, $J$ = 7.5 Hz, 2 H), 8.00 (s, 4 H), 3.65 (s, 6 H), 2.45 (s, 6 H). $^{13}$C NMR ($CDCl_3$) $\delta$ 160.6, 149.2, 140.4, 137.0, 136.0, 130.9, 125.1, 114.3, 61.5, 22.0. MS (MALDI-TOF) $m/z$ 567 [M + H]$^+$. HRMS (MALDI-FT) calcd for $C_{30}H_{27}N_6O_6$ [M]$^+$ 567.1987, found 567.1985.

**Compound 11:** To a solution of 2-fluoro-3-(methoxycarbonyl)-benzoic acid[27] (1.00 g, 5.52 mmol) in THF (20 mL) were added oxalyl dichloride (2.0 mL, 25 mmol) and DMF (0.1 mL). The solution was stirred at room temperature for 0.5 h and then concentrated in vacuo. The resulting pale yellow solid **10** was dissolved in THF (30 mL). This solution was then added dropwise to a stirred solution of **5** (1.09 g, 2.77 mmol) and triethylamine (4 mL) in THF (30 mL), which was cooled in an ice-bath. Stirring was continued for 1 h and the solution concentrated under reduced pressure. The resulting residue was triturated with chloroform (30 mL). After workup, the crude product was purified by column chromatography (hexane/AcOEt 2:1 to 3:2) to afford **11** as a white solid (1.45 g, 70%). $^1$H NMR ($CDCl_3$) $\delta$ 8.83 (d, $J$ = 16.2 Hz, 2 H), 8.33 (t, $J$ = 7.5 Hz, 2 H), 8.26 (d, $J$ = 6.6 Hz, 2 H), 8.13 (t, $J$ = 7.2 Hz, 2 H), 3.99 (t, $J$ = 0.9 Hz, 6 H), 3.44 (s, 2 H), 3.24 (s, 2 H), 1.34−1.18 (m, 20 H), 0.88 (s, 3 H), 0.79 (s, 3 H). $^{13}$C NMR ($CDCl_3$) $\delta$ 169.9, 164.0, 164.0, 161.2, 160.7, 157.7, 136.7, 136.2, 133.9, 133.8, 126.1, 125.9, 124.8, 124.7, 122.4, 122.2, 119.8, 119.7, 116.3, 53.0, 52.8, 52.5, 49.4, 45.3, 31.8, 31.7, 31.6, 29.4, 29.3, 29.1, 28.7, 27.5, 27.2, 26.7, 22.7, 22.6, 14.1, 14.0. $^{19}$F NMR ($CDCl_3$) $\delta$ −112.1 (d, t, $J_1$ = 16.8 Hz, $J_2$ = 6 Hz, 2 F), −144.2 (s, 1 F). MS (MALDI-TOF) $m/z$ 754.5 [M + H]$^+$. Anal. Calcd for $C_{41}H_{50}F_3N_3O_7$: C, 65.32; H, 6.69; N, 5.57. Found: C, 65.55; H, 6.79; N, 5.46.

By using a similar procedure, compound **15** was prepared in 65% yield as white solid from **5a** and **14**.[28] $^1$H NMR ($CDCl_3$) $\delta$ 10.36 (s, 2 H), 8.47 (d, $J$ = 8.1 Hz, 2 H), 8.36−8.30 (m, 4 H), 8.10 (t, $J$ = 7.8 Hz, 2 H), 4.07 (s, 6 H), 3.48 (t, $J$ = 7.8 Hz, 2 H), 3.27 (t, $J$ = 7.8 Hz, 2 H), 1.67−1.59 (m, 4 H), 1.37−1.12 (m, 20 H), 0.88 (t, $J$ = 6.6 Hz, 6 H). $^{13}$C NMR ($CDCl_3$) $\delta$ 170.0, 164.7, 161.3, 149.5, 146.8, 145.6, 142.3, 139.0, 134.1, 134.0, 127.8, 126.1, 126.0, 125.6, 115.4, 53.1, 49.4, 45.3, 31.8, 29.4, 29.3, 29.1, 28.7, 27.6, 27.2, 26.7, 22.7, 14.1, 1.0. $^{19}$F NMR ($CDCl_3$) $\delta$ −144.1 (s, 1 F). MS (ESI) $m/z$ 720.3 [M + H]$^+$. Anal. Calcd for $C_{39}H_{50}FN_5O_7$: C, 65.07; H, 7.00; N, 9.73. Found: C, 65.05; H, 7.02; N, 9.63.

**Compound 12:** A solution of **11** (1.25 g, 1.66 mmol) and lithium hydroxide (0.24 g, 10.0 mmol) in water (50 mL) and THF (10 mL) was stirred at room temperature for 2 h. Hydrochloric acid (2 N) was added dropwise to pH 5 and then the mixture was concentrated under reduced pressure. The resulting residue was suspended in water (5 mL). The precipitate formed was filtered, washed with water, and recrystallized from ethanol to give **12** as a white solid (1.14 g, 95%). $^1$H NMR ($CDCl_3$) $\delta$ 8.94 (d, $J$ = 20.4 Hz, 2 H), 8.47−8.42 (m, 4 H), 8.24 (t, $J$ = 7.5 Hz, 2 H), 7.40 (t, $J$ = 7.5 Hz, 2 H), 3.49 (s, 2 H), 3.27 (s, 2 H), 1.38−1.19 (m, 24 H), 0.92 (s, 3 H), 0.78 (s, 3 H). $^{13}$C NMR (DMSO-$d_6$) $\delta$ 168.9, 164.6, 162.6, 159.1, 157.0, 134.1, 132.7, 128.9, 128.2, 125.9, 125.4, 124.4, 120.2, 119.0, 48.6, 44.4, 31.2, 28.6, 28.5, 28.1, 27.0, 26.4, 25.9, 22.0, 13.9. $^{19}$F NMR ($CDCl_3$) $\delta$ −111.3 (s, 2 F), −147.2 (s, 1 F). MS (ESI) $m/z$ 726.3 [M + H]$^+$. Anal. Calcd for $C_{39}H_{46}F_3N_3O_7 \cdot 0.5H_2O$: C, 63.75; H, 6.45; N, 5.72. Found: C, 63.77; H, 6.25; N, 5.55.

**Compound 16:** $^1$H NMR ($CDCl_3$) $\delta$ 10.40 (s, 2 H), 8.35 (d, $J$ = 7.8 Hz, 2 H), 8.21 (d, $J$ = 7.2 Hz, 2 H), 8.03−7.96 (m, 4 H), 3.57 (t, $J$ = 6.0 Hz, 2 H), 3.28 (t, $J$ = 4.5 Hz, 2 H), 1.65−1.64 (m, 4 H), 1.30−1.10 (m, 24 H), 0.85−0.75 (m, 6 H). $^{13}$C NMR ($CDCl_3$) $\delta$ 169.3, 165.2, 162.1, 162.0, 148.8, 147.1, 145.4, 140.8, 133.6, 128.1, 126.1, 118.9, 48.9, 44.8, 31.7, 29.0, 28.5, 27.5, 26.9, 26.3, 22.5, 14.3. $^{19}$F NMR ($CDCl_3$) $\delta$ −137.0 (s, 1 F). MS (ESI) $m/z$ 692 [M + H]$^+$. HRMS (ESI) calcd for $C_{37}H_{47}N_5O_7F$ [M]$^+$ 692.3454, found 692.3455. Anal. Calcd for $C_{37}H_{46}FN_5O_7 \cdot H_2O$: C, 62.61; H, 6.82; N, 9.87. Found: C, 62.25; H, 7.02; N, 9.73.

**Compound 13:** To a solution of **12** (0.65 g, 0.89 mmol) in THF (20 mL) were added oxalyl dichloride (1.0 mL, 12 mmol) and DMF (0.1 mL). The solution was stirred at room temperature for 0.5 h and then concentrated. The resulting pale yellow solid was dissolved in THF (30 mL) and the solution added slowly to a stirred solution of **5a** (1.65 g, 2.67 mmol) and triethylamine (2 mL) in THF (30 mL) at °C. The solution was stirred for 1 h and concentrated under reduced pressure. The resulting residue was triturated with chloroform (30 mL). After workup, the crude product was purified by column chromatography (*n*-hexane/AcOEt 3:2) to afford **13** as a pale yellow solid (0.80 g, 60%). $^1$H NMR ($CDCl_3$) $\delta$ 9.15 (d, $J$ = 4.5 Hz, 2 H), 8.85 (d, $J$ = 10.2 Hz, 2 H), 8.25 (d, $J$ = 4.8 Hz, 2 H), 8.15−8.10 (m, 4 H), 7.67 (s, 2 H), 7.37 (t, $J$ = 6.9 Hz, 2 H), 6.59 (d, $J$ = 5.4 Hz, 2 H), 3.43−3.22 (m, 12 H), 1.04−1.00 (m, 72 H), 0.89 (s, 9 H), 0.82 (s, 9 H). $^{13}$C NMR ($CDCl_3$) $\delta$ 170.9, 170.1, 161.3, 160.9, 159.5, 156.1, 144.0, 140.8, 135.1, 134.9, 133.5, 133.3, 126.2, 126.1, 125.9, 125.7, 125.1, 123.1, 123.0, 122.8, 116.5, 111.3, 109.8, 60.4, 49.5, 49.2, 45.3, 45.0, 31.8, 31.7, 29.7, 29.4, 29.3, 29.1, 28.6, 27.4, 27.1, 26.6, 22.7, 22.6, 21.0, 14.1. $^{19}$F NMR ($CDCl_3$) $\delta$ −114.2 (s, 2 F), −142.7 (s, 1 F), −150.1 (s, 2 F). MS (MALDI-TOF) $m/z$ 1499.0 [M + Na]$^+$. HRMS (MALDI-TOF) calcd for $C_{85}H_{123}N_9O_7F_5$ [M]$^+$ 1476.9460, found 1476.9483.

By using a similar procedure, compound **17** was prepared from **16** and **5** (4 equiv) as a white solid in 60% yield. $^1$H NMR ($CDCl_3$) $\delta$ 10.00 (s, 2 H), 9.79 (s, 2 H), 8.46 (d, $J$ = 7.2 Hz, 2 H), 8.41 (d, $J$ = 8.1 Hz, 4 H), 8.08 (t, $J$ = 7.8 Hz, 2 H), 7.71 (d, $J$ = 5.4 Hz, 2 H), 6.43 (d, $J$ = 7.2 Hz, 2 H), 3.79 (s, 4 H), 3.34 (s, 6 H), 3.19 (s, 6 H), 1.65−1.50 (m, 12 H), 1.42−1.21 (m, 36 H), 1.18−1.01 (m, 18 H). $^{13}$C NMR ($CDCl_3$) $\delta$ 175.1, 171.2, 170.0, 161.0, 160.9, 148.9, 148.3, 143.6, 140.5, 139.7, 135.8, 135.7, 134.0, 133.6, 125.9, 125.7, 125.5, 125.3, 114.9, 111.9, 107.9, 49.4, 45.3, 45.1, 31.9, 31.8, 30.7, 29.7, 29.6, 29.5, 29.3, 29.1, 28.7, 27.7, 27.2, 26.7, 22.7, 22.6, 17.7, 14.1. $^{19}$F NMR ($CDCl_3$) $\delta$ −148.7 (s, 1 F), −153.8 (t, $J$ = 33.0 Hz, 2 F). MS (MALDI-FT) $m/z$ 1443.5 [M + H]$^+$. HRMS (MALDI-TOF) calcd for $C_{83}H_{123}N_{11}O_7F_3$ [M]$^+$ 1442.9535, found 1442.9547.

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**Supporting Information Available:** General experimental procedures, UV−vis and fluorescent spectra of partial complexes, the simulated diffusion decay curves of **1**, **1** + $C_{60}$, and **1** + $C_{70}$, $^1$H NMR spectra of new compounds, and CIF files of **3**, **4**, and **15**. This material is available free of charge via the Internet at http://pubs.acs.org.

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